

Fluorescence quenching in dyes under an optically thin approximation

GEORGE C CHENNATTUCHERRY*, G AJITHKUMAR and
N V UNNIKRISHNAN

School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam 686 560, India

*Department of Physics, St. Berchmans' College, Changanacherry 686 101, India

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Abstract. Kinetic analysis of the energy level scheme of a dye molecule yields expression for the fluorescence quantum yield. The quantum yield is dependent on molecular parameters and laser pulse characteristics. Calculations show quenching of fluorescence quantum yield due to excited state absorption. Earlier studies on quenching of fluorescence have been discussed quantitatively under an optically thin approximation.

Keywords. Energy level scheme; fluorescence quantum yield; excited state absorption.

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1. Introduction

Many workers, in an attempt to determine optimum configurations for nitrogen laser pumped tunable dye lasers, described that some dyes operate efficiently whether pumped transversely [1] or longitudinally [2] whereas others operate efficiently only in the transversely excited mode [3]. The primary differences between the two modes of excitation appear to be linked to the quenching of dye fluorescence yield at high pump intensity. This effect called photoquenching [4] comes about when molecules in their excited state absorb a photon. This photon, in general, through a radiationless process, is converted into heat and therefore does not contribute to the yield. This effect will usually be much more important at laser type intensities where other nonlinear processes can be neglected [5, 6]. In this report, expressions have been derived for the intensity dependent quantum yield and general nature of the yield on molecular parameters and laser characteristics has been discussed. Moreover, the results are discussed in relation to previous experiments on the fluorescence quenching of 7-DAMC and rhodamine 6G dye molecules.

2. Kinetic analysis and fluorescence yield

The energy level (figure 1) scheme represents the singlet manifold of a large molecule. The state X_1 can be excited at the rate $k_{12} = \sigma_{12}I$, σ_{12} being the absorption cross section at the exciting laser frequency and I is the laser intensity. The excitation is to some vibronic level X'_2 which relaxes at a rate k_{vib} into all other states X_2 . The state X_2 can decay back to X_1 with a decay rate $k_{21} = k'_{21} + k''_{21}$, where k'_{21} and k''_{21} are the radiative and nonradiative decay rate constants respectively. Depending on

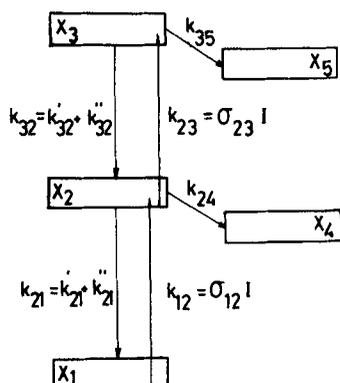


Figure 1. Kinetic energy level scheme for a dye molecule.

the value of the absorption cross section σ_{23} , the induced transition $X_2 \rightarrow X_3$ can compete with the $X_2 \rightarrow X_1$ decay process. This will be true as long as the pulse duration $\Delta t \gg 1/k_{\text{vib}}$ and the intensity satisfies the condition $\sigma_{12} I \ll k_{\text{vib}}$ so that stimulated emission from X_2' can be neglected. We will focus our attention to the situation where the laser pulses obey these relationships and the rate constants k_{24} and k_{35} for the intersystem crossing are negligibly small.

For calculation of the total fluorescence yield, the coupled differential equations corresponding to figure 1 in the optically thin approximation can be written in the matrix form

$$KX = dX/dt \quad (1)$$

or more explicitly, for the fluorescence case

$$\begin{bmatrix} -k_{12} & k_{21} & 0 \\ k_{12} & -(k_{21} + k_{23}) & k_{32} \\ 0 & k_{23} & -k_{32} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \frac{d}{dt} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}. \quad (2)$$

Equation (2) can be solved analytically [7] by defining the concentration $X_i = A_i \exp(-\lambda t)$, here the A_i are constants and λ is a parameter to be determined. The corresponding set of algebraic equations for the A_i has a nontrivial solution only when the condition

$$\det(K_{ij} - \delta_{ij} \lambda) = 0 \quad (3)$$

is satisfied.

The resulting equation has the solutions

$$\lambda_1 = 0, \lambda_2 = 1/2(p + q), \lambda_3 = 1/2(p - q) \quad (4)$$

where

$$\begin{aligned} p &= (k_{12} + k_{21} + k_{23} + k_{32}), \\ q &= [p^2 - 4(k_{12}k_{23} + k_{12}k_{32} + k_{32}k_{21})]^{1/2}. \end{aligned} \quad (5)$$

The general solutions for the X_i are determined using the conditions $x_0 = x_1 + x_2 + x_3$

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for any time t and $x_0 = x_1 (t = 0)$ and thus we obtain

$$x_2 = x_0 k_{12} \left[\frac{k_{32}}{\lambda_2 \lambda_3} + \frac{k_{32} - \lambda_2}{\lambda_2 (\lambda_2 - \lambda_3)} \exp(-\lambda_2 t) + \frac{\lambda_3 - k_{32}}{\lambda_3 (\lambda_2 - \lambda_3)} \exp(-\lambda_3 t) \right], \quad (6)$$

$$x_3 = x_0 k_{12} k_{23} \left[\frac{1}{\lambda_2 \lambda_3} + \frac{\exp(-\lambda_2 t)}{\lambda_2 (\lambda_2 - \lambda_3)} - \frac{1}{\lambda_3 (\lambda_2 - \lambda_3)} \exp(-\lambda_3 t) \right]. \quad (7)$$

The total number of fluorescence photons emitted per molecule from states X_2 and X_3 is given by $Y = Y_2 + Y_3$ where

$$Y_2 = k'_{21} \left[\int_0^{\Delta t} (x_2/x_0) dt \right] + k'_{21} [x_2(\Delta t) + x_3(\Delta t)]/k_{21} x_0 \quad (8)$$

and

$$Y_3 = k'_{32} \left[\int_0^{\Delta t} (x_3/x_0) dt \right] + k'_{32} x_3(\Delta t)/k_{32} x_0 \quad (9)$$

with x_2 and x_3 are the molecular concentration in states X_2 and X_3 and x_0 is the total concentration.

Following the method developed [4] for excitation by a square shaped pulse of duration Δt , the integration can be performed yielding

$$Y_2 = \frac{k'_{21} \sigma_{12} I}{k_{21}} \left[\frac{k_{21} k_{32} \Delta t + k_{32} + k_{21} + \sigma_{23} I}{\lambda_2 \lambda_3} - \frac{k_{21} k_{32} (\lambda_2 + \lambda_3)}{\lambda_2^2 \lambda_3^2} + \frac{(\lambda_2 - k_{32})(k_{21} - \lambda_2) + \lambda_2 \sigma_{23} I \exp(-\lambda_2 \Delta t)}{\lambda_2^2 (\lambda_2 - \lambda_3)} + \frac{(\lambda_3 - k_{32})(\lambda_3 - k_{21}) - \lambda_3 \sigma_{23} I \exp(-\lambda_3 \Delta t)}{\lambda_3^2 (\lambda_2 - \lambda_3)} \right] \quad (10)$$

and

$$Y_3 = \frac{k'_{32} \sigma_{12} \sigma_{23} I^2}{k_{32}} \left[\frac{\Delta t k_{32}}{\lambda_2 \lambda_3} - \frac{k_{32} (\lambda_2 + \lambda_3)}{\lambda_2^2 \lambda_3^2} + \frac{(\lambda_2 - k_{32}) \exp(-\lambda_2 \Delta t)}{\lambda_2^2 (\lambda_2 - \lambda_3)} + \frac{(k_{32} - \lambda_3) \exp(-\lambda_3 \Delta t)}{\lambda_3^2 (\lambda_2 - \lambda_3)} \right] \quad (11)$$

where

$$k_{12} = \sigma_{12} I \quad \text{and} \quad k_{23} = \sigma_{23} I. \quad (12)$$

For cases where the transmission of the system is intensity independent, the quantum yield is given by

$$\phi = Y/\sigma_{12} I \Delta t. \quad (13)$$

Thus ϕ is intensity dependent. It approaches the intensity independent form for low

intensities.

$$\text{Limit } I \rightarrow 0 \phi = \phi_0 = k'_{21}/k_{21} \quad (14)$$

A steady state is obtained for pulses of duration $\Delta t \gg 1/k_{ij}$.

Using (5), (6), (10) and (11) we find for the steady state limit of Y

$$Y = \frac{(k'_{21}k_{32} + k'_{32}\sigma_{23}I)\sigma_{12}I\Delta t}{\sigma_{12}\sigma_{23}I^2 + k_{32}\sigma_{12}I + k_{21}k_{32}}. \quad (15)$$

For cases where a steady state approximation is applicable, it is useful to derive an expression for Y and for an n -level system of the type



A straightforward calculation yields the following expression. The concentration x_i of the state X_i

$$x_i = \alpha_i x_0 / \sum_{i=1}^n \alpha_i \quad (17)$$

so that

$$\sum_{i=1}^n x_i = x_0$$

where

$$\alpha_i = I^{i-1} \prod_{j=1}^{n-1} k_{j+1,j} \prod_{j=1}^{i-1} \sigma_{j,j+1}/k_{j+1,j}$$

for

$$i = 2, 3, \dots, n \quad (18)$$

and

$$\alpha_i = \prod_{j=1}^{n-1} k_{j+1,j}. \quad (19)$$

The yield per molecule is

$$Y = \sum_{i=2}^n k'_{i,i-1} (x_i/x_0) \Delta t = \left(\sum_{i=2}^n k'_{i,i-1} \alpha_i \right) \Delta t \sum_{i=1}^n \alpha_i \quad (20)$$

The number of photons absorbed per unit volume in an optically thin sample is

$$N_{\text{abs}} = \sum_{i=1}^{n-1} \sigma_{i,i+1} I x_i \Delta t = x_0 I \Delta t \sum_{i=1}^{n-1} \sigma_{i,i+1} \sum_{i=1}^n \alpha_i. \quad (21)$$

Thus the quantum yield becomes

$$\phi = x_0 Y/N_{\text{abs}} = \sum_{i=2}^n k'_{i,i-1} \alpha_i / \sum_{i=1}^{n-1} \sigma_{i,i+1} \alpha_i. \quad (22)$$

If the radiative lifetime of higher levels is larger than that of the lower ones, a maximum in the fluorescence as a function of laser intensity will be observed. For the three level case in steady state, this maximum in Y occurs when $\sigma_{12}\sigma_{23}I^2 = k_{21}k_{32}$ [8].

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Equation (15) which was derived analytically for the time dependent case could also be obtained from equation for $n = 3$. Moreover, from (18) and (19) we obtain

$$\sigma_{i,i+1} \alpha_i / \sigma_{i+1,i+2} \alpha_{i+1} = k_{i+1,i} / \sigma_{i+1,i+2} I \quad (23)$$

If for all $i \geq 2$ the intensity is such that $k_{i+1,i} \gg \sigma_{i+1,i+2} I$ then the n -level case reduces to the three level case. For instance, then

$$\begin{aligned} \phi &= (k'_{21} \alpha_2 + k'_{32} \alpha_3) / (\sigma_{12} \alpha_1 + \sigma_{23} \alpha_2) \\ &= (k'_{21} k_{32} + k'_{32} \sigma_{23} I) / k_{32} (k_{21} + \sigma_{23} I) \end{aligned} \quad (24)$$

which is also obtained using (22), (15), (16) and (17) for $\Delta t \rightarrow \infty$.

For low intensities, $\sigma_{23} I \ll k_{32}$ and usually $k'_{21} \approx k'_{32}$ so that the following expression is obtained for the reciprocal relative quantum yield

$$\phi_0 / \phi \approx 1 + \sigma_{23} I / k_{21}. \quad (25)$$

Plotting ϕ_0 / ϕ versus I at low intensities should give a straight line with a slope equal to σ_{23} / k_{21} . If the fluorescence lifetime of the state X_2 is known its absorption cross-section can be determined or vice versa.

3. Calculations and quantum yield of 7-DAMC

Fluorescence yields were calculated using eqs (5) and (10)–(13) for various combinations of the molecular parameters k_{32}/k_{21} and for different excitation conditions. For a given laser pulse, the yield Y shows the expected dependence on the molecular parameters. For instance, for fixed $I\Delta t$ and $\sigma_{23} = \sigma_{12}$, Y decreased with increasing k_{32}/k_{21} . However, the general dependence of Y and ϕ on I and Δt does not change much with the molecular parameters. Hence the calculation performed for the case of $k_{32}/k_{21} = 10$ is taken as typical (figure 2).

The calculations show that the steady state is reached for practically all pulses of duration $\Delta t > 5/k_{21}$. Therefore, for most molecular systems steady state approximation

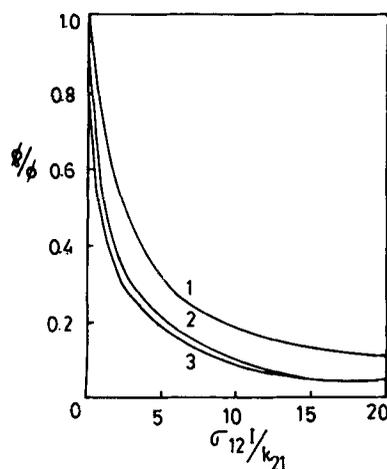


Figure 2. Dependence of quantum yield on laser intensity $k_{32}/k_{21} = 10$ and $\sigma_{12} = \sigma_{23}$. (Curve 1. $\Delta t k_{21} = 1.0$; Curve 2. $\Delta t k_{21} = 5$; Curve 3. $\Delta t k_{21} = 10.0$.)

can be used to analyse laser-induced fluorescence process. The quantum yield calculated as a function of incident laser intensity is shown in figure 2. A strong quenching effect due to excited state absorption is observed for $\Delta t \cdot k_{21} > 5$ and more which indicates that more quenching is obtained for longer pulses. These effects appear to be a clear consequence of the low intensity values where steady state approximation holds good.

An experimental verification of the I dependence of ϕ is found in dye laser studies of Wieder [6]. Wieder's experiment was performed on 7-DAMC solution in ethanol using a nitrogen laser (337.1 nm) at a maximum intensity of 200 MW/cm². Since the laser pulse duration was 5 ns a steady state was reached in practice. From Wieder's data, a plot of the reciprocal relative quantum yield ϕ_0/ϕ versus I can be made. The result is shown in figure 3. It can be seen that a straight line is obtained for low I at the two concentrations. Further, the straight line type behaviour for 3×10^{-5} mol/l dye concentration exactly fits with (25). Even though one notices a similar behaviour for 5×10^{-5} mol/l concentration also, this does not follow strictly (25). This is due to the fact that the former concentration is optically thin while the latter is not. Therefore, we measured the slope of the 3×10^{-5} mol/l case, and find that $\sigma_{23}/k_{21} = 3 \times 10^{-26}$ cm²s. In Wieder's experiment the transmission was intensity independent. $\sigma_{23} = \sigma_{12} = 1.67 \times 10^{-17}$ cm², thus $k_{21} = 3.01 \times 10^8$ s⁻¹ a reasonable value. The reciprocal of k_{21} , gives the lifetime of 3.33 ns which agrees well with the

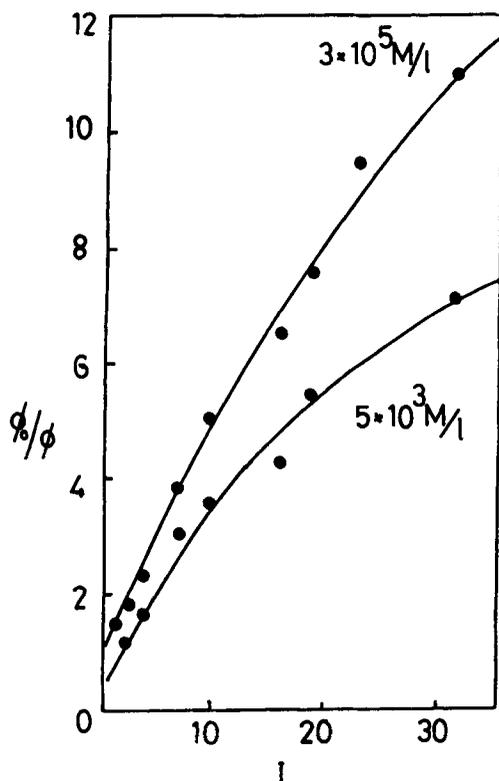


Figure 3. Reciprocal relative quantum yield of 7-DAMC as a function of N₂-laser intensity. Data are taken from ref. [6].

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reported value of 3.5 ns [9]. The curvature of the plots at high intensities is due to the failure of the approximation $\sigma_{23}I \ll k_{32}$.

4. Fluorescence quenching in 7-DAMC and rhodamine 6G

Under the optically thin approximation, we have also analysed Wieder's data on fluorescence quenching. The analysis helps one to get a quantitative estimate of the competitive deexcitation process responsible for fluorescence quenching. For fluorescent molecules in an excited state, the fraction of molecules that radiate in the presence of competitive deexcitation process is given by

$$f = P_R \left(P_R + \sum_c P_c \right)^{-1} \quad (26)$$

P_R is the spontaneous transition probability and $\sum_c P_c$ gives the sum total of the probabilities of competitive processes. In case absorption from the first excited singlet state is the dominant deexcitation process, then the effect on the fraction of the molecules should be a term $P_c = CI^x$ where I is the intensity of the pump radiation and C is a constant. We have then

$$I^x = \frac{P_R}{C} (1/f - 1) \quad (27)$$

Using the approximation [eqs (10) and (11)] we have examined the validity of this expression. Figure 4 shows the theoretical plot of $\log(1/f - 1)$ vs $\log I$ along with Wieder's plots for the two dyes. The theoretical and experimental curves show a slope of nearly unity as expected. However there is a large discrepancy between the

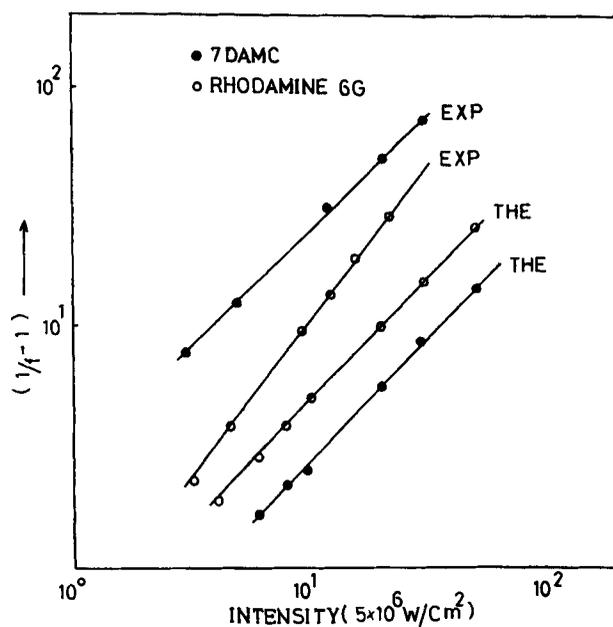


Figure 4. $\log(1/f - 1)$ vs $\log I$ plot.

theoretical and experimental curves. This could be explained by considering the following three important photophysical processes. Firstly, fluorescence quenching would result if the relaxation from the higher excited states to the X_2 state is less efficient than the X_3 to X_2 relaxation. Secondly, stimulated emission from X_2 to X_1 would also produce an additional intensity dependent fluorescence quenching. Thirdly, it is also likely that thermal heating may contribute to the quenching processes under high intensity excitation. It must be emphasized that too much reliance cannot be placed on fitting experimental results, where gaussian pulse has been used to the square pulse model theoretical curves. The general agreement on the nature of the experimental curves and theoretical curves of the square pulse approximation used indicates that this is a useful approximate theoretical model at least for understanding the general behaviour of the intensity dependence fluorescence quenching. Thus considering the general agreement on the nature of the experimental and theoretical curves the discrepancy between curves would be due to the above mentioned processes. Hence we cannot expect an exact fit between theoretical and experimental results. Moreover, a comparison of the two plots for the two dyes shows that rhodamine 6G has high quantum yield consistent with previous observations [2]. The probability of deexcitation process has been estimated to be of the order of $10^8/s$ and is found to increase with laser intensity except for a numerical factor.

5. Conclusions

1. It has been shown that the fluorescence quantum yield is a decreasing function of the pulse width for a given pump intensity. 2. The kinetic calculation is found to be applicable to optically thin systems and at lower laser intensities. 3. Fluorescence yields are of no value, unless they have been extrapolated to zero laser intensity. 4. Estimate of quantum yield and deexcitation probability shows that, in particular, excited state absorption should be a good competitor for the fluorescence emission.

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